The Isotopic Exchange Between Some Organometric Compounds and Metallic Mercury Labelled by Hg203

topic exchange does not proceed over a state of equilibrium, but the metallic mercury directly reacts with the organomercuric R-HgX salt. Although the reaction probably is homolytic, it hardly proceeds over the stage of the formation of free radicals. The maintenance of the stereochemical configuration at the carbon atom which is connected with the mercury atom also speaks against the formation of free radicals. There are 1 table, and 4 references, 3 of which are Slavic.

association:

State University imeni M. V. Loucaces (Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova)

PRESENTED:

October 26, 1957, by A. N. Nesmeyanov, Academician

SUBMITTED:

October 24, 1957

AVAILABLE:

Library of Congress

Card 3/3

PHASE I BOOK EXPLOITATION

858

Reutov, Oleg Aleksandrovich, Professor

Novyye sinteticheskiye materialy (New Synthetic Materials) Moscow, Izd-vo "Znaniye", 1958. 29 p. (Series: Vsesoyuznoye obshchestvo po rasprostraneniyu politicheskikh i nauchnykh znaniy. Seriya IV, 1958, No. 13) 86,000 copies

Sponsoring Agency: Vsesoyuznoye obshchestvo po rasprostraneniyu politicheskikh i nauchnykh znaniy.

Ed.: Faynboym, I.B.; Tech. Ed.: Trofimova, A.V.

This popular booklet is for the general reader.

COVERAGE: This pamphlet informs the reader on the new synthetic materials which PURPOSE: play an important role in industry, technology, and in everyday life. Three main types of synthetics are discussed: rubber, plastics, and synthetic fibers. The basic characteristics of these materials are described as well as the fields of their application.

Card 1/2

	858	
New Synthetic Materials		
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PHASE I BOOK EXPLOITATION

SOV /2917

Reutov, Oleg Aleksandrovich, Corresponding Member, USSR Academy of Sciences

Organicheskiy sintez i yego perspektivy (Organic Synthesis and Prospects for Its Development) Moscow, Gostekhizdat, 1958. 95 P. (Series: Nauchno populyarnaya hiblioteka) 500,000 copies printed.

Ed.: S.A. Shorygin; Tech. Ed.: A.P. Kolesnikova.

This popular science booklet is intended for students and persons interested in the chemistry and technology of organic synthesis. PURPOSE:

COVERAGE: This booklet explains the basic principles of organic chemistry and organic synthesis. Major products of synthesis are listed and the importance of carbon as the basic element of numerous chemical products is emphasized. Products obtained from coal and petroleum are discussed, and the role of natural gas and refinery gas in the production of synthetic material is explained. The production of synthetic rubber, fiber, resins, plastics, and drugs is briefly outlined. The author also reviews discoveries of Russian chemists such as A.M. Butlerov, N.N. Zinin, N.D. Zelinskiy, and M.G. Kucherov. In conclusion he notes the progress made in the field of synthetic material production, and points to further achievements. No references are given.

card 1/3

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REDITOV, C. A., OSTAPCHUK, G. M., U Yan-Tsey, SMOLINA, T. A. and KMOL', P., (Moscow State University in M. V. Lomonosov)

"The Use of Radioactivey Mercury Hg for Studying the Exchange Reactions at a Carbon Atom." $_{7}, _{2}, _{3}$

Isotopes and Radiation in Chemistry, Collection of papers of 2nd All-Union Sci. Tech. Conf. on Use of Radioactive and Stable Isotopes and Radiation in National Economy and Science, Moscow, Izd-vo AN SSSR, 1958, 380pp.

This volume published the reports of the Chemistry Section of the 2nd AU Sci Tech Conf on Use of Radioactive and Stable Isotopes and Radiation in Science and the National Economy, sponsored by Acad Sci USSR and Main Admin for Utilization of Atomic Energy under Council of Miniasters USSR Moscow 4-12 Apr 1957.

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AUTHORS:

sov/156-58-1-27/46

TITLE:

Reutov. O. A., Ptitsyna, O. A., Karpov, T. P., Smolina, T. A. On the Reaction of the Isotope Exchange Between Tri-Aryl-Stibines and Radioactive Antimony Sb124(0 reaktsii izotopnogo

obmena mezhdu triarilstibinami i radioaktivnoy sur moy Sb124)

PERIODICAL:

Nauchnyye doklady vysshey shkoly, Khimiya i khimicheskaya tekhnologiya, 1958, Nr 1, pp. 115 - 116 (USSR)

ABSTRACT:

The authors recently investigated the reactions of the type

 $Ar_nE + E \Longrightarrow Ar_nE + E (I)$

(in which case E - is an n-valent element and E - its radioactive isotope). These reactions are the most simple models for reactions between metalorganic compounds and free metals (as well as some non-metals); they are the basis of one of the most important methods of synthesis of the metalorganic compounds (Ref 1): $mAr_n Me + nE \longrightarrow nAr_m + mMe$ (II)(in which case Me - is

an n-valent metal and E - an m-valent metal). Naturally, the rules which were determined with the exchange-reactions of the type (I) may be of considerable importance for the further development of the method of synthesis according to scheme (II).

Card 1/3

On the Reaction of the Isotope Exchange Between Tri- SOV/156-58-1-27/46 Aryl-Stibines and Radioactive Antimony Sb124

The exchange reaction Ar3Sb + Sb Ar3Sb + Sb referred to in the title, takes place under rather severe conditions. Only when boiling a tetralin solution of triphenyl-stibine (at 207°) with a radioactive antimony powder, a 17% exchange took place within 5 hours. The petroleum fraction with a boiling temperature of from 190 to 2000 was used as indifferent solvent in further tests. Tri-p-tolyl stibine was used as test naterial. Considerable divergences were observed in spite of several parallel tests: the equilibrium was established once at a 15%, once at a 30% and another time at an 80% exchange. Since the surface area of the metallic antimony forms one of the most important factors of the exchange. These diverging results indicate that this surface is in any way changed in the course of the reaction. Apparently, a recrystallization of the antimony powder takes place during its heating in petroleum at from 190 to 2000 which is ended within approximately 30 hours. The estimation of surface area of a "reprepared" and a not reprepared radioactive antimony powder shows 1,44 m²/s and 6,9 m2/6 respectively. The interaction of the "reprepared" radio-

Card 2/3

On the Reaction of the Isotope Exchange Between Tri-SOV/156-58-1-27/46 Aryl-Stibines and Radioactive Antimony Sb124

> active antimony with tri-p-tolyl stibine in parallel tests lead to a conforming equilibrium exchange (15 to 16%) within 80 to 100 hours. There are 3 references, 2 of which are Soviet.

ASSOCIATION: Kafedra organicheskoy khimii Moskovskogo gosudarstvennogo univer-

siteta im.M.V.Lomonosova (Chair of Organic Chemistry at the

Moscow State University imeni M.V.Lomonosov)

SUBMITTED: October 26, 1957

Card 3/3

CIA-RDP86-00513R001444710019-0 "APPROVED FOR RELEASE: 06/20/2000

sov/156-58-2-30/48 Reutov, O. A., Smolina, T. A., ATTHORS: Wu Yang -ch'i Bubnov, Yu. N.

Isotopic Exchange of Several Organomercury Salts and Mercury Haloid Labelled by Hg203(Izotopnyy obmen nekotorykh 203) rtutnoorganicheskikh soley s galoidnoy rtut'yu, mechenney Hg203) TITLE:

Nauchnyye doklady vysshey shkoly. Khimiya i khimicheskaya tekhnologiya, 1958, Nr 2, pp. 324 - 327 (USSR) PERIODICAL:

In continuation of previous papers the authors investigated ABSTRACT:

the interaction between the mercury mentioned in the title and: α-mercury bromo-cyclohexane, the ethyl- and 1-methylether of the α -mercury bromo-phenyl acetic acid, 3-mercury bromo-camphor, 3-benzyl-3-mercury bromo camphor, 1-mercury chloro-camphenylon, 2-mercury bromo camphane, and n.butylmercury bromide. The organomercury salts which are (except 1-mercury chloro-camphenylon) exo-compounds, react under mild conditions with mercury haloid. From the results (Table 1) appears that the reactivity of the investigated organomercury salts is reduced with respect to mercury haloid in a certain

order (scheme given). 1-mercury bromo-camphenylon, 2-mercury

Card 1/3

Isotopic Exchange of Several Organomercury Salts and SOV/156-58-2-30/48 Mercury Haloid Labelled by Hg²⁰³

bromo camphane, and n.butyl-mercury bromide do not enter into the reaction of the isotopic exchange under these conditions. When the authors compared the results obtained by the reactions in benzene and dioxane to those in acetone they found that admixtures are contained in acetone which are not removed in the case of a normal dehydration. They are assumed to be responsible for the considerable fluctuations of the rate of reaction observed in acetone. The authors were able to prove that the reaction of the isotopic exchange is considerably accelerated by acids as well as by bases. It is possible that the bases lead to a solvation of the mercury atom and thus weaken the C-Hg bond. The influence of acids is probably specific only for the cases of the α-mercurized oxo-compounds. The hydrogen of the acid probably influences the oxygen of the carbonyl group. This weakers the C-Hg bond. Apparently the isotopic exchange in question is a bimolecular reaction of the electrophilic substitution at the saturated carbon atom (S_E 2). Further investigations in this respect are necessary. An experimental part follows. There are 1 table

Card 2/3

Isotopic Exchange of Several Organomercury Salts and SOV/156-58-2-30/48 Mercury Haloid Labelled by Hg203

and 1 reference, which is Soviet.

ASSOCIATION: Kafedra organicheskoy khimii Moskovskogo gosudarstvennogo universiteta im.M.V.Lomonosova (Chair of Organic Chemistry of the Moscow State University imeni M.V.Lomonosov)

SUBMITTED:

October 28, 1957

Card 3/3

19 SOV/55-58-3-23/30 5(3) Reutov, O.A. and Lovtsova, A.N. AUTHORS: The Arylation of the Trichlorides of Diarvlantimony by Salts of the Diaryliodonium (Arilirovaniye trekhkhloristoy diaril-TITLE: sur'my solyami diariliodoniya) Vestnik Moskovskogo universiteta, Seriya matematiki, meknaniki, 1958,Nr 3,pp 191-196 (USSR) PERIODICAL: astronomii, fiziki, khimii The cleavage of the binary iodonium salts of the trichloride of diarylantimony and of the mixtures of diaryliodonium ABSTRACT: chloride and diarylantimony-trichloride by zinc powder in acetone was investigated. It was stated that triaryle antimonous organic combinations arise thereby. There are 1 table, and 7 references, 3 of which are Soviet, 3 American, and 1 German. Kafedra organicheskoy khimii (Chair of Organic Chemistry) ASSOCIATION: June 17, 1957 SUBMITTED: Card 1/1

"Neue Darstellun Chemische Techni	gsmethode	Antimonor	ganischer	Verbindur	nreri, II		
Chemische Techni	<u>k</u> , Nol 4,	Apr 1958.					
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sov/156-58-4-36/49

AUTHORS:

Reutov, O. A., Beletskaya, I. P., Filipponko, L. R.

TITLE:

The Symmetrization of Mercury-Organic Salts by Means of Diphenyl Mercury (Simmetrizatsiya rtutnoorganicheskikh soley s

pomoshch'yu difenilrtuti)

PERIODICAL:

Nauchnyye doklady vysshey shkoly. Khimiya i khimicheskaya

tekhnologiya, 1958, Nr 4, pp 754-756 (USSR)

ABSTRACT:

In the interaction of mercury-organic salts with mercury diphenyl, symmetric mercury-organic compounds are formed in
great yield. The following mercury-organic salts were prepared:
acetcnyl-mercury chloride, ethyl ester of the α-bromo mercury
phenyl acetic acid, ethyl ester of the n-bromo-α-bromo mercury
phenyl acetic acid, 3-bromo-mercury-3-benzyl camphor and transchloro-vinyl-mercury chloride. The mechanism of the symmetrization of the mercury-organic salts proceeds according to the

fcllowing scheme: $2R_1 R_2 R_3 CHgX \rightleftharpoons (R_1 R_2 R_3 C)_2 Hg + HgX_2$

HgX2 + (C6H5)2Hg - 2C6H5HgX.

There are 1 table and 5 references, 4 of which are Soviet.

Ca There are 1 tab

Chair of Organic Chen, Moscow State U.

15

5(3)

AUTHORS:

TITLE:

Reutov, O.A., Lu Chin-chu

SOV/55-58-5-17/34

Bundel', Yu.G.

Synthesis of Some Optically Active Mercury-Organi Compounds

of the Terpene Series (Sintez nekotorykh opticheski aktivnykh

rtutnoorganicheskikh soyedineniy ryada terpenov)

PERIODICAL:

Vestnik Monskovskogo universiteta, Seriya matematiki, mekhaniki, astronomii, fiziki, khimii, 1958, Mr 5, pp 111 - 118 (USSE)

ABSTRACT:

Mercurated derivatives of camphane and of menthane of the type R HgX and R2Hg were synthetically produced, where R denotes

bornyl, isobornyl or 1-menthyl. Diastereomers of 2-chlorecourcamphane were obtained in pure state which differ from each other only by the configuration in the second carbon atom. The main properties, particularly the crystallographic ones are given. The motive for the present paper were the investigations of A.N. Nesmeyanov. The method of I.A. Kondakov and I.A. Shindel'mayzer [Ref 5] was used.

Chr. of Organic Chem

AUTHOR:

Reutow ... O ...

sov/62-58-6-5/37

TITLE:

The Investigation of Electrophile and Homolytic Reactions of Substitution in the Carbon Atom by the Method of Isotope Exchange (Issledovaniye elektrofil'nykh i gomoliticheskikh reaktsiy zameshcheniya u atoma ugleroda metodom izotopnogo obmena) Lecture Delivered at the General Meeting of the Department of Chemical Sciences AS USSR, on December 19, 1957 (Doklad na obshchem sobranii otdeleniya khimicheskikh nauk Akademii nauk SSSR 19 dekabrya 1957 g.)

PERIODICAL:

Izvestiya Akademii nauk SSSR, Otdeleniye khimicheskikh nauk, 1958, Nr 6, pp. 684-692 (USSR)

ABSTRACT:

In the course of the investigation of the mechanism of the electrophile and homolytic reactions of substitutions in saturated carbon atoms (shown by the example of mercury-organic compounds) (Refs 1 - 6) the authors employed the method of isotope exchange. The following reactions of isotope exchange were systematically investigated:

 $R - Hg - R + Hg \longrightarrow R - Hg - R + Hg$

Card 1/3

SQV/ 62-50-6-5/37

The Investigation of Electrophile and Homolytic Reactions of Substitution in the Carbon Atom by the Method of Isotope Exchange. Lecture Delivered at the General Meeting of the Department of Chemical Sciences AS USSR on December 19, 1957

$$R - Hg - X + Hg \xrightarrow{\longrightarrow} R - Hg - X + Hg$$

$$R - Hg + X + HgX_2 \xrightarrow{\longrightarrow} R - Hg - X + HgX_2$$

(R = Ar, Alk or C1CH=CH; X=Cl or Br. The radioactive mercury isotope Hg²⁰⁸ was used). Results obtained: Diaryl mercury and aryl mercury chlorides, enter into reaction (of isotope exchange) with metallic mercury Hg²⁰³ (under weak conditions). Electropositive substituents in para-position of the benzene ring facilitate reaction, but electronegative substituents render it more difficult. The homolytic reactions under investigation develop immediately between the molecules of the mercury-organic compounds and the molecules of mercury. Moreover, the dependence of the reaction velocities of the isotope exchange of the mercury organic salts (of the cyclic and alicyclic series with metallic mercury and sublimate) upon the structural factors (and additions of acid) was investigated. The homolytic and electrophile reactions of the isotope exchange of mercury-organic salts develop in such a

Card 2/3

307/62-58-6-5/37

The Investigation of Electrophile and Homolytic Reactions of Substitution in the Carbon Atom by the Method of Isotope Exchange. Lecture Delivered at the General Meeting of the Department of Chemical Sciences AS USSR on December 19, 1957

> manner that the configuration is contained in saturated carbon. By investigating the isotope exchange of isomeric β-chlorovinyl mercury-organic compounds (with Hg and HgCl2) the direct proof was obtained of the correctness of the rule (set up by Nesmeyanov and Borisov) concerning the maintenance of stereochemical configuration in the olefine atom of carbon. There are 1 figure, 2 tables, and 15 references, 12 of which are Soviet.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova

(Moscow State University imeni M.V. Lomonosov)

SUBMITTED:

February 28, 1958

2. Substitution reactions 1. Carbon--Exchange reactions

3. Mercury chlorides -- Exchange reactions 4. Mercury isotopes

--- Exchange reactions

Card 3/3

5(3) AUTHORS:

Nesmeyanov, A. N., Reutov. O. A.,

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SOV/62-58-11-7/26

Loseva, A. S., Khorlina, M. Ya.

TITLE:

Synthesis of Organo-Mercury Compounds From Hydrazones (Sintez rtutnoorganicheskikh soyedineniy iz gidrazonov)
Communication I. Interaction of Hydrazones of Aliphatic
Aldehydes and Ketones With Mercury Acetate (Soobshcheniye 1.

Vzaimodeystviye gidrazonov al'degidov i ketonov alifaticheskogo ryada s uksusnokisloy rtut'yu)

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,

1958, Nr 11, pp 1315-1326 (USSR)

ABSTRACT:

Earlier, hydrazones - a group of easily accessible compounds - have not been used for the synthesis of organometallic compounds. It is demonstrated in the present paper that the reaction of hydrazones of acetaldehyde, acetone, methyl-ethyl ketone, and butyrone with mercury acetate in aqueous methanol and absolute benzene medium may serve for the production of some new types of organo-mercury compounds. The reaction investigated takes place according to that of a "conjugated compound" under participation of the medium.

Card 1/3

∞, ~ dimercury or ∞, ~ , ß, ß'-tetramercury ether form in

Synthesis of Organo-Mercury Compounds From Hydrazones. SOV/62-58-11-7/26 Communication I. Interaction of Hydrazones of Aliphatic Aldehydes and Ketones With Mercury Acetate

water, ≪-mercury or ∞, /3-dimercury alkyl methyl esters in methanol, and & -mercury or &, \beta-dimercury alkyl acetates in absolute benzene. The chemical properties of the obtained organo-mercury compounds were investigated. It is demonstrated that a) dimercury compounds of the type (IV) - (VI) are decomposed by concentrated hydrochloric acid when heated. In this connection they separate calomel and form the corresponding carbonyl compounds b) bromination of dimercury compounds of the type (IY) - (VI) with a bromine solution saturated with potassium bromide leads in the cold to the formation of a corresponding &-bromoketone at the same time with a ketone c) monomercury compounds of the type (I) - (III) are decomposed in the cold by concentrated alkali. On this occasion they separate metallic mercury and form the corresponding carbonyl compounds. There are 1 table and 10 references, 2 of which are Soviet.

ASSOCIATION: Card 2/3

Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova (Moscow State University imeni M. V. Lomonosov)

5(3) AUTHORS:

Nesmeyanov, A. N., Reutov, U. A.,

SOV/62-58-11-8/26

Wu Yang-ts'u, Lu Ching-chu

TITLE:

On the Problem of the Stereochemistry of the Reaction Between Symmetric Organo-Mercury Compounds and Mercury Halide (K voprosu o stereokhimii reaktsii simmetrichnykh rtutnoorganicheskikh soyedineniy s galoidnoy rtut'yu)

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,

1958, Nr 11, pp 1327-1330 (USSR)

ABSTRACT:

In the present paper the authors investigated the stereochemistry of the reaction of symmetric &-mercury-1-menthyl ester of phenyl-acetic acid and mercury bis-&,&-camphor with mercury bromide in acetone solution. Both reactions represent an electrophilic substitution with saturated carbon atoms. It was demonstrated that the first reaction in the cold takes place under maintenance of the configuration at the touched carbon atom. Racemization observed at 56° is a secondary process. Stereochemistry of the reaction of mercury bis-&,&-camphor

Card 1/2

with mercury bromide could not be determined because the forming 3-bromomercury camphor racemizes under the action

On the Problem of the Stereochemistry of the Reaction Between Symmetric Organo-Mercury Compounds and Mercury Halide

SOV/62-58-11-8/26

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of mercury bromide during the reaction even in the cold. By the investigation of the reaction of symmetric &-mercury-1-menthyl ester with an equimolecular amount of hydrogen bromide the conclusions which had already been drawn (Ref 1) were confirmed. Conclusions: the reaction in the course of which the organo-mercury salts become symmetric under the action of ammonia takes place at the saturated carbon atom under maintenance of the configuration. There are 4 references, 3 of which are Soviet

ASSOCIATION:

Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova (Moscow State University imeni M. V. Lomonosov)

CHARLEMAN

SUBMITTED: March 26, 1957

Card 2/2

CIA-RDP86-00513R001444710019-0 "APPROVED FOR RELEASE: 06/20/2000

5(3) AUTHORS:

Nesmeyanov, A. N., Reutov, O.A. Ptitsyna, O. A., Tsurkan, P. A.

SOV/62-58-12-6/22

TITLE:

Synthesis of Organometallic Compounds of Pentavalent Antimony by Arylation of the Organic Antimony Compounds ArSbX, and Ar SbX by Diazo-Compounds (Sintez metalloorganicheskikh soyedineniy pyativalentnoy sur'my putem arilirovaniya sur myanocrganicheskikh soyedineniy $ArSbX_2$ i Ar_2SbX

diazosoyedineniyami)

PERIODICAL.

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1958, Nr 12, pp 1435-1444 (USSR)

ABSTRACT:

Published works give little data on the arylation of organic antimony compounds by means of diazo-compounds (Refs 4-7). In the present paper the authors investigated in detail the possibilities of arylating compounds of the type ArSbX and Ar SbX by means of diazo-compounds as well

as of various diazonium double salts. They succeeded in

Card 1/3

finding such conditions under which the reaction of arylation can be carried out easily and in good yield. The method based

Synthesis of Organometallic Compounds of SOV/62-58-12-6/22 Pentavalent Antimony by Arylation of the Organic Antimony Compounds ArSbX and Ar_SbX by Diaze-Compounds

on the action of diazonium double salts of antimony trichloride on aryl-diadc stibine proved to be a universal method for the synthesis of mixed organic antimony compounds of the type ArAr'SbX₃. The former are easily obtained from aryl stibine exides. In almost all cases the reaction takes place at low temperatures and leads to the formation of the corresponding organic antimony compounds in very good yields. The compounds ArAr'SbX₃ were isolated as diaryl antimonic acid and identified as the diazonium double salts ArAr'SbCl₃ · Ar''N₂Cl according to the method developed in reference 9:

ArAr'Sb <u>elocholic HCl</u> ArAr'SbCl₃

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Synthesis of Organometallic Compounds of SOV/62-58-12-6/22 Pentavalent Antimony by Arylation of the Organic Antimony Compounds ArSbX and Ar₂SbX by Diazo-Compounds

ArAr'SbCl₃ + Ar"N₂Cl · FeCl₃ → ArAr'SbCl₃ · Ar"N₂Cl + FeCl₃.

The results obtained are given in a table. The preparation method employed in synthesizing the substances of the types ArAr'SbX₃ and Ar₂Ar'SbX₂ is an important supplement of previous methods (Refs 2, 8-11) for the production of compounds of this type. There are 1 table and 16 references, 9 of which are Soviet.

ASSOCIATION:

Moskovskiy gosudarstvennyy universitet imeni M. V. Lomonosova (Moscow State University imeni M. V. Lomonosova)

SUBMITTED:

March 26, 1957

Card 3/3

REUTOV, O.A.; LOVTSOVA, A.N.

Arylation of diarylantimony trichloride with diaryliodonium salts. Vest. Mosk.un. Ser.mat., mekh., astron., fiz.khim. 13 no.3: 191-196 '58. (MIRA 12:4)

1. Kafedra organicheskoy khimii Moskovskogo universiteta. (Arylation) (Antimony compounds)

(Iodonium compounds)

AUTHORS: Reutov, O. A., Ptitsyna, O. A., Patrina, N. D. 79-28-3-5/61

TITLE: Double Diazo Salts of Stannic Trichloromethyl and of Stannic

Dichlorodiethyl (Dvoynyye diazoniyevyye soli trekhkhloristogo

metilolova i dvukhloristogo dietilolova)

PERIODICAL: Zhurnal Obshchey Khimii, 1958, Vol. 28, Nr 3, pp. 588-592

(USSR)

ABSTRACT: According to a method for the synthesis of double diazo salts

of antimony organic compounds (ref. 4) elaborated by one of the authors earlier, the authors in the present work carried out the synthesis of the double diazo salts of stannic trichloromethyl. These salts were synthetized by pouring together in the cold an aceton solution of the freshly produced ArN₂Cl.FeCl₃-salt with the methyl alcohol

solution of CH₂SnOOH which was saturated with hydrogen chloride: CH₂SnOOH + 3HCl → CH₃SnCl₃ + 2H₂O, 2ArN₂Cl.FeCl₃ +

+ $CH_3SnCl_3 \rightarrow (ArN_2Cl)_2.CH_3SnCl_3 + 2FeCl_3$. The salts

Card 1/3 ($C_6H_5N_2C1$)₂. CH_3SnCl_3 and $(p-C_7H_7N_2C1)_2CH_3SnCl_3$, and others

Double Diazo Salts of Stannic Trichloromethyl and of Stannic 79-28-3-5/61 Dichlorodiethyl

could not be obtained in this way. Therefore an one-step method for the synthesis of the diazo salts of stannic trichloromethyl was elaborated as follows: the chloride solution of $\mathrm{CH}_{\mathrm{Z}}\mathrm{SnOOH}$ was added to a diazo solution which had been obtained by diazotizing an aromatic amine in hydrochloric acid by means of sodium-nitrite - this immediately leading to a precipitate of (ArW2Cl)3.CH3SnCl3-salt. The use of o--toluidine did not furnish any diazo salt. The double diazo salts of stannic trichloromethyl obtained according to either method are mentioned in table 1. In the synthesis of the double diazo salts (C2H5)SnCl2 another method had to be used: the chloride of the amine was dissolved in alcohol and then diazotized with isoamylnitrite. The stannic dichlorodiethyl dissolved in alcohol was then added to the diazo solution. The formation of the double salt (C2H5)2SnCl2 can be represented by the following reaction process:

Card 2/3

Double Diazo Salts of Stannic Trichloromethyl and of Stannic 79-28-3-5/61 Dichlorodiethyl

synthetized this way are mentioned in table 2. There are

2 tables and 5 references, 4 of which are Soviet.

ASSOCIATION:

Moskovskiy gosudarstvennyy universitet

(Moscow State University)

SUBMITTED:

February 7, 1957

Card 3/3

CIA-RDP86-00513R001444710019-0 "APPROVED FOR RELEASE: 06/20/2000

20-1-28/58 Mesmeyanov, A. N., Academician Reutov, O. A., Knoll', P. The Employment of the Isotopic Method in Studying the Stereochemistry of Replacement Reactions at the Olefinic Carbon Atom (Izucheniye TITLE: stereokhimii reaktsiy zameshcheniya u olefinovogo atoma ugleroda s pomoshch yu izotopnogo metoda). Doklady AN SSSR, 1958, Vol. 118, Nr 1, pp. 99-102 (USSR). PERIODICAL: Together with Borisov the first author (reference 1) established the following rule: electrophile and homolytic replacement reactions ta-ABSTRACT? ke place under conversation of the cis- and trans-configuration. This rule was derived in the study of the metal exchange in the series of stereoisomeric organometallic compounds of the type? By employing the method of isotopes the authors in this paper directly proved the correctness of this rule. As example of electrophile reactions they studied the interaction of trans-and cis-β-

Card 1/3

The Employment of the Isotopic Method in Studying the 20-1-28/58 Stereochemistry of Replacement Reactions at the Olefinic Carbon Atom.

chlorovinyl_mercury chloride with sublimate labelled with radioactive mercury Hg203. The reactions were carried out in an acetone solution in the cold. In both cases the isotopic equilibrium was soon obtained (within 5 minutes). The stereochemical initial configuration of the chlorovinyl group was on that occasion strictly conserved. As homolytical reactions they studied the interaction of metallic mercury labelled with Hg with trans and cis-8-chlorovinylmercury chlorides, as well as that with bis trans and bis cisβ-chlorovinyl-mercury. All h above-mentioned organo-mercury compounds readily react in acetone in the cold with finly distributed metallic mercury. The isotopic equilibrium is attained after some hours. The configuration of the chlorovinyl groups is always conserved in this connection. During the interaction of the metallic mercury with trans- and cis-\$-mercuryvinylchlorides a side reaction takes place under formation of calomel and acetylene. This is an example of the double reactivity which is so very characteristic of all \$_chloro= vinyl-organometallic compounds. The two electrophile and the two first homolytical reactions require an additional discussion. The observed stereochemistry of these 4 reactions was not the result of one but of several processes. It may be stated that these i reac-

Card 2/3

The Employment of the Isotopic Method in Studying the Stereochemistry 20-1-28/58 of Replacement Reactions at the Olefinic Carbon Atom.

tions do not proceed over the equilibrium, but that HgCl_2 and Hg directly react with the β -chlorovinyl-mercury chlorides. Thus the results obtained here are a direct proof of the conservation of the configuration at the olefinic carbon atom during the electrophile and homolytical replacement reactions. An experimental part with the usual data follows.

There are 4 references, 3 of which are Slavic.

ASSOCIATION: Moscow State University imeni M.V. Lomonsov. (Moskovskiy gosudarst-

vennyy universitet imeni M. V. Lomonosova).

SUBMITTED: October 22, 1957.

AVAILABLE. Library of Congress.

Card 3/3

SOV/20-120-5-34/67 Rentov. C. A., Encll', P., Yan-Tsey U AUTHORS: On the Stereochemistry of the Isotopic Exchange Reactions TITLS: Between Crganomercuric Salts and Metalle or Halogen Mcrcury Labelled With Hg (O stereokhimii reaktsiy izotornogo obmena rtutnoorganicheskikh soley s metallicheskoy i galoidnoy rtut'yu, mechennymi Hg²⁰³) Doklady Akademii nauk Siich, 1958, Vol. 1220, Nr 5, pp. 1052-1055 PERIODICAL: (usan) The authors explain the stereochemistry of the following reactions: $H_1\dot{H}_2\dot{H}_3\dot{C}$ - $Hg\dot{X}$ + Hg \longrightarrow $H_1\dot{H}_2\dot{H}_3\dot{C}$ - $Hg\dot{X}$ + HgABSTRACT: $R_1 R_2 R_3 C - HgX + HgX_2 \longrightarrow R_1 R_2 R_3 C - HgX + HgX_2$ Heaction (1) represents the process of a homolytical reaction, (2) that of an electrophilic substitution at the saturated carbon atom. In the present paper the stereochemistry of reaction (1) is investigated on the basis of the diastomeric 1-methyl-ether of the mercury bromide phenyl acetic acid. Reaction (2) is explained on the basis of the cis- and trans isomer of the 2-methoxy-cyclohexyl-mercury chloride. Both Card 1/3

On the Stereochemistry of the Troiopic Exchange Reactions Between Organomerourie Salts and Me allicor Halogen Mercury Labelled With Eg

diastomers of the first substance react easily with atomized mercury at cold in a medium of absolute benzene. The sterecmetric configuration at the a-carbon atom is in either case entirely conserved: the rotation angles of the diastomers before the reaction and after the establishment or the isotopic equilibrium were identical. This is another proof that these homolytical reactions are no free-radical-reactions, otherwise the reaction would be bound to lead to a racemization. The molecules of the organomercury compounds apparently react directly with the mercury molecules. Cis- and trans-2--methoxy-cyclohexyl-mercuric chlorides were chosen in order to clear the reaction stereochemistry. The reaction of the isotopic exchange was carried out in dioxane, acetone, and ischutyl alcohol. It proceeds with a noticeable velocity only at 120-135. In all cases the initial stereochemical configuration of the substances was entirely maintained. The same results were obtained with all other investigated reactions of the electrophilic substitution at the saturated

Card 2/3

SOV/20-120-5-34/67 On the Stereocnemistry of the Isotopic Exchange Reactions Between Organomercuric Salts and Metalke or Halogen Mercury Labelled With Hg 203

> carbon atom, except the cases reported by Cram (Kram, Ref 5) There are 5 references, 4 or which are Soviet.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova (Moscow State University imeni M. V. Lomonosov)

FRESENTED:

February 26, 1958, by A. N. Mesmeyanov, Member, Academy of Sciences, USSR

SUBMITTED:

February 26, 1958

1. Mercury isotopes--Exchange reactions 2. Mercury compounds (Organic) -- Exchange reactions 3. Mercury salts -- Exchange reactions 4. Mercury compounds (Labeled) -- Exchange reactions 5. Stereochemistry

Card 3/3

AUTHORS:

Nesneyanov, Nik. A., Reutov, O. A.

20-120-6-28/59

CONTROL OF STREET OF STREE

TITLE:

Functional Derivatives of Ferrocene-1,1 Dicarboxylic Acid

(Funktsional nyye proizvodnyye ferrotsen-1,1'-dikarbonovoy kisloty)

PERIODICAL:

Doklady Akademii nauk SSSR, 1958, Vol 120, Nr 6,

pp 1267 - 1270 (USSR)

ABSTRACT:

Although the acid mentioned in the title was produced already in 1952 (Ref 1) its derivatives remained unknown with two exceptions (Refs 1,2). In the present paper the authors obtained a number of these derivatives. They are: a) the chlorine anhydride b) from the latter an amide (V) was produced,:c) methyl ether of the carbamido-ferrocene-10-carboxylic acid (VII); d) the above amides (V), and (VII) as well as the amide of ferrocene carboxylic acid can be converted into the corresponding nitriles by heating in acetic anhydride. By heating the acid (VII) at 140 for 20 minutes e) 1-cyano ferrocene-1'-carboxylic acid (VIII) formed in a yield of 55%; f) the nitrile of ferrocene-1,1'-dicarboxylic acid (IX) was obtained in a yield of 30% by heating the amide of this acid in acetic anhydride at 100° during 6 hours; g) by heating the amide of ferrocene carboxylic acid in acetic anhydride at 140° during 40 minutes the nitrile of this

Card 1/8

Functional Derivatives of Ferrocene-1,1'-Dicarboxylic 20-120-6-28/59 Acid

> acid formed (X); h) a cleavage of the HCl elements from the 2 chlorine anhydride molecules as well as from 2 water molecules takes place under the formation of the anhydride of the ferrocene-1,11dicarboxylic acid (XI) due to the action of pyridine on chlorine anhydride (IV) in the presence of water. Constants are given of all substances mentioned and their structure is discussed. According to the aromatic character of ferrocene it was found that the radical -CCl3 may replace one of the ferro-

cene hydrogens. In spite of the variation of the decomposition conditions of trichloroacetic acid in the mixture with ferrocene no products of a double trichloromethylation of ferrocene could be observed. There are 1 table and 7 references, 3 of which are Soviet.

ASSOCIATION:

Moskovskiy gosudarstvennyy universitet im. M.V. Lomonosova (Moscow State University imeni M.V. Lomonosov)

PRESENTED:

February 11, 1958, by A.N. Nesmeyanov, Member, Academy of Sciences, USSR

Card 2/

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CIA-RDP86-00513R001444710019-0 "APPROVED FOR RELEASE: 06/20/2000

5(2), 5(3)

AUTHORS:

Reutov, O. A., Corresponding Member, SOV/20-122-5-21/56 Academy of Sciences, USSR, Ptitsyna, O. A., Khu Khun-Ven

TITLE:

The Synthesis of Organomercuric Compounds by Means of

Diaryl Iodonium Salts (Sintez rtutnoorganicheskih soyedineniy

cherez soli diarilyodoniya)

PERIODICAL:

Doklady Akademii nauk SSSR, 1958, Vol 122, Nr 5,

pp 825-827 (USSR)

ABSTRACT:

As was formerly proved by the authors (Refs 1, 2), the double salts of diaryl iodonium can serve as a source for the production of organo-metallic compounds of tin, antimony and bismuth. The reaction consists of a decomposition of diaryl iodonium double salts by tin, antimony or bismuth powders, respectively. The paper under review deals with the possibility of applying this reaction to the synthesis of organomercuric compounds. In order to find optimum conditions, the authors decomposed the corresponding double salt of diphenyl-iodonium chloride sublimate in various solvents. Hg, Fe, Zn, Cu and Ag were used as reducing factors. The results are given in table 1. They show that the main product of reaction is diphenyl mercury

Card 1/2

The Synthesis of Organomercuric Compounds by Means of Diaryl Iodonium Salts

SOV/20-122-5-21/56

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when iron is used. In all other cases it was C6H5HgCl. Silver decomposes the double salt (C6H5)2JCl.HgCl2 by forming diphenyl-iodonium chloride and calomel; no organomercuric compounds are created. The maximum yield of phenyl mercury chloride is obtained in the decomposition of the double salt of diphenyl-iodonium chloride sublimate by mercury in water. Because of various short-comings in the use of silver salts, the authors decided to use diphenyl iodonium salts for the synthesis of organomercuric compounds. As can be seen in table 3, a high yield of organomercuric compounds is formed by means of diaryl iodonium salts. Also the comparatively easy accessibility of these salts, as well as the simple process of the synthesis speak in favor of the method suggested. There are 3 tables and 4 references, 2 of which are Soviet.

SUBMITTED:

July 5, 1958

Card 2/2

CIA-RDP86-00513R001444710019-0 "APPROVED FOR RELEASE: 06/20/2000

5(1, 2) AUTHORS:

Reutov. O. A., Corresponding

SOV/20-122-6-21/49

Member, AS USSR, Ptitsyna, O. A., Styazhkina, N. B.

TITLE:

Decomposition of Asymmetric Diaryliodonium Salts by Bismuth Powder in the Presence of Bismuth Trichloride (Razlozheniye nesimmetrichnykh soley dierilyeleniya

poroshkom vismuta v prisutstvii trekhkhloristogo vismuta)

PERIODICAL:

Doklady Akademii nauk SSSR, 1958, Vol 122, Nr 6,

pp 1032-1034 (USSR)

ABSTRACT:

The first two authors have demonstrated in an earlier paper (Ref 1) that in the decompositon of the diaryliodonium chlorides by tin powder in the presence of tin dichloride organotin compounds are formed in good yield. Furthermore it was demonstrated that in the decomposition of unsymmetric salts of diaryliodonium of the type ArAr'JCl under same conditions the more intensely electronegative radical passes from iodine to tin. All these reactions obviously pass through the preliminary stage of the formation of double iodonium salts of tin dichloride, which are decomposed by tin powder.

Card 1/3

In the same paper (Ref 1) the possibility of forming organobismuth compounds was shown. They are formed by

Decomposition of Asymmetric Diaryliodonium Salts by SOV/20-122-6-21/49 Bismuth Powder in the Presence of Bismuth Trichloride

decomposition of double salts of diaryliodonium chloride and of bismuth trichloride by bismuth powder. For reasons of preparation it has turned out to be more practical not to decompose a double salt by bismuth but to decompose a mixture of Ar2JCl and BiCl3. For example, the yield of triphenyl bismuth will be 35-40 % under these conditions. The reactions taking place in connection with this are explained by equations. The unsymmetric salts decomposed by the method described are given in table 1 together with the substances produced in this process. As can be seen from it, the more intensely electronegative radical passes in all cases to bismuth. In no case it was possible to isolate a second substance. Apparently it is formed in such small quantities which could only be detected by means of chromatography, e. g. The results obtained are difficult to understand as the quantity of the electron density does not represent a determinative factor in radical reactions (Ref 1), even if it is maintained that the decomposition of double radicals takes place "homolytically". At the same time the regularity observed here in the transition

Card 2/3

Decomposition of Asymmetric Diaryliodonium Salts by SOV/20-122-6-21/49 Bismuth Powder in the Presence of Bismuth Trichloride

of the more intensely electronegative radical to the metal can easily be explained by the assumption of a heterolytic decomposition of the iodonium double salts. Although in recent times more and more knowledge of a certain role of the polar factors in the radical reactions has been collected, all data described by the authors give evidence of the heterolytic mechanism of the decomposition reactions of the iodonium salts which are discussed here. There are 1 table and 6 references, 1 of which is Soviet.

SUBMITTED:

July 5, 1958

Card 3/3

NESMEYANOV, Aleksandr Nikolayevich, akademik; REUTOV, O.A., otv.red.toma;
TOPCHIYEV, A.V., akademik, red.; KNUNYANTS, I.L., akademik, red.;
KABACHNIK, M.I., akademik, red.; FREYDLINA, R.Kh., red.; KAN, B.I.,
red.; LOSKUTOVA, I.P., red.izd-va; POLYAKOVA, T.V., tekhn.red.

[Selected works in four volumes] Izbrannye trudy v chetyrekh tomakh. Moskva, Izd-vo Akad.nauk SSSR. Vol.1. 1959. 712 p. (MIRA 12:12)

1. Chleny-korrespondenty AN SSSR (for Reutov, Freydlina).
(Chemistry)

"Formation Mechanism of the Metal-Carbon Compound and Some Aspects of the Reaction Capacity of Metal Organic Compounds of Heavy Metals."

report to be submitted at the 17th International Congress of Pure and Applied Chemistry - Munich, GFR, 30 Aug - 6 Sep 1959.

CIA-RDP86-00513R001444710019-0 "APPROVED FOR RELEASE: 06/20/2000

5(3)

SOV/62-59-1-8/38

AUTHORS:

Nesmeyanov, A. N., Reutov, O. A., Loseva, A. S.,

Khorlina, M. Ya.

TITLE:

Synthesis of Organo-Mercury Compounds From Hydrazones (Sintez rtutnoorganicheskikh soyedineniy iz gidrazonov) Communication 2. Interaction of Hydrazones of the Aldehydes and Ketones of the Alicyclic and Aromatic Series With Mercury (II) Acetate (Soobshcheniye 2. Vzaimodeystviye gidrazonov al'degidov i ketonov alitsiklicheskogo i aromatiches-

kogo ryadov s uksusnokisloy rtut'yu)

PERIODICAL:

Otdeleniye khimicheskikh nauk, Izvestiya Akademii nauk SSSR.

1959, Nr 1, pp 50 - 61 (USSR)

ABSTRACT:

In the present paper the authors have shown that the hydrazones of aldehydes and ketones of the alicyclic and aromatic series (hydrazones of cyclohexanone, 4-methyl cyclohexanone, cyclopentanone, camphor, benzophenone and o-nitro-benzaldehyde) react with mercury (II) acetate in water, methanol and absolute bensene and separate nitrogen, mercury (I) acetate and metallic mercury, and form organo-mercury compounds. In most cases the reaction under the action of

Card 1/

Synthesis of Organo-Mercury Compounds From Hydrazones. SOV/62-59-1-8/38 Communication 2. Interaction of Hydrazones of the Aldehydes and Ketones of the Alicyclic and Aromatic Series With Mercury (II) Acetate

the solvent takes place in the way mentioned in Ref 1 . The reaction of hydrazones of cyclohexanone and 4-methyl cyclohexanone with mercury (II) acetate in water and in the presence of catalytic quantities of copper acetate is very peculiar. As a result of this interaction organomercury compounds with a double bond are formed. Organomercury compounds are listed in the table which were synthesized by way of hydrazones of the allcyclic and aromatic series. The structure of the organo-mercury compounds obtained was confirmed by decomposition with concentrated alkali or concentrated hydrochloric acid (Ref 1). The hydrazones used in this paper were synthesized according to methods already described: hydrazone of cyclohexanone (Ref 2), of 4-methyl cyclohexanone (Ref 3), of camphor (Ref 4), of benzophenone (Ref 5) and o-nitro-benzaldehyde (Ref 6). There are 1 table and 14 references, 2 of which are Soviet.

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Card 2/3

5(3) AUTHOR: Reutov, O. A., Corresponding Member AS USSRSOV/30-59-1-28/57

TITLE:

Symposium on Theoretical Organic Chemistry (Simpozium po

teoreticheskoy organicheskoy khimii)

PERIODICAL:

Vestnik Akademii nauk SSSR, 1959, Nr 1, pp 114 - 115 (USSR)

ABSTRACT:

This symposium was held in memory of A. Kekule in London from September 15 until September 17, 1958. It had been organized by the British Chemical Society and the Department of Organic Chemistry of the International Association for Theoretical and Applied Chemistry. 600 chemists from 25 countries participated. 3 lectures and 15 reports were heard. All mentioned reports were held by western scientists.

Card 1/1

sov/156-59-1-35/54 Ptitsyna, C. A., Reutov, C. A., Turchinskiy, M. F. 5(3) AUTHORS: The Decomposition of Asymmetric Salts of Diaryl Iodonium by Tin Powder in the Presence of Tin Dichloride (Razlozheniye TITLE: nesimmetrichnykh coley diariliodoniya poroshkom olova v prisutstvii dvukhloristogo olova) Nauchnyye doklady vysskey shkoly. Khimiya i khimickeskaya tekhnologiya, 1959, Nr 1, pp 138 - 140 (USSR) PERIODICAL: A method for the synthesis of organic tin compounds is presented. The following compounds were treated with tin powder ABSTRACT: in the presence of tin chloride: c₆H₅(p-cH₃OC₆H₄)JC1 → (c₆H₅)₂SnO, $c_6^{H_5}(m-c_2^{H_5} \circ coc_6^{H_4}) Jc1 \rightarrow (m-c_2^{H_5} \circ coc_6^{H_4})_2 Sn0, \text{ yield } 40\%$ $(p-cH_3oc_6H_4)(p-c_2H_5ococ_6H_4)Jc1 \rightarrow (p-c_2H_5ococ_6H_4)_2SnC$, yield $(o-CH_{3}C_{6}H_{4})(p-CH_{3}C_{6}H_{4})JC1 \rightarrow (o-CH_{3}C_{6}H_{4})_{2}SnO, yield 53\%$ Card 1/2

The Decomposition of Asymmetric Salts of Dieryl Iodonium SCV/156-59-1-35/54 by Tin Powder in the Presence of Tin Dichloride

The compounds obtained and their yields are listed in a table. In all cases, the more electro-negative radical attached itself to the tin. No tin compounds were obtained on the decomposition of iodonium salts containing nitrogroups. In these compounds intensive resinification occurred which may be due to reduction processes of the nitro-groups, The experimental part of the paper presents the reaction details, as well as those of the production of the iodonium salts, with regard to laboratory work. There are 1 table and 5 references, 2 of which are Soviet.

ASSOCIATION:

Kafedra organicheskoy khimii Moskovskogo gosudarstvennogo universiteta im. M. V. Lomonosova (Chair of Organic Chemistry of Moscow State University imeni M. V. Lonchosov)

SUDMITTED:

July 10, 1958

Card 2/2

CIA-RDP86-00513R001444710019-0 "APPROVED FOR RELEASE: 06/20/2000

5(4) AUTHORS: Reutov. O. A., Smolina, T. A.,

sov/62-59-3-33/37

Hu Hung-weng

TITLE:

None Given

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,

1959, Nr 3, pp 559-560 (USSR)

ABSTRACT:

In this letter to the editor the authors write: We have found that organic mercury compounds may enter the reaction of an isotopic exchange of the following type under soft conditions:

R2Hg + R2Hg - R2Hg + R2Hg . In pyridine the half period of exchange in the reaction of equimolecular amounts of diphenyl mercury with di-p-chlorophenyl mercury (concentration

of the substances - 0.03 mol/1) at 60° is 3 hours.

 $(c_6H_5)_2Hg + (clc_6H_4)_2Hg = (c_6H_5)_2Hg + (clc_6H_4)_2Hg$. At room temperature di-p-chlorophenyl mercury in acetone solution with mercury-bis-acetaldehyde - a substance with an extremely reactive mercury atom - does not enter the reaction of isotopic exchange. In the interaction between diphenyl mercury and

Card 1/2

sov/62-59-3-33/37

mercury-bis-acetaldehyde, however, the isotopic equilibrium in acetone is practically immediately produced at room temperature. The same holds also for di-p-anisyl mercury.

(CH₃OC₆H₄)₂Hg + Hg (CH₂-C)_H = (CH₃OC₆H₄)₂Hg + Hg (CH

At present there are no data available which would allow a definite judgement of the mechanism of the discovered isotopic exchange. It may be assumed that the reaction is not free-radical because free radicals cannot form from organic mercury compounds under such soft conditions.

ASSOCIATION:

Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova (Moscow State University imeni M. V. Lomonosov)

SUBMITTED:

November 17, 1958

Card 2/2

5(3) AUTHORS: Reutov, O. A., Uglova, E. V.

SOV/62-59-4-39/42

TITLE:

Letters to the Editor (Pis'ma redaktoru)

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,

1959, Nr 4, p 757 (USSR)

ABSTRACT:

The authors write in this letter: "The possibility of the existence of a constant stereochemical configuration of the carbon atom combined with metal in the case of the molecule having a single asymmetrical center has as yet not been experimentally proved. We were successful in proving it by separating for the first time the racemic mercury salts 2-bromomercury butane and 5-bromomercury-2-methylhexane in antipodes. Alkylmercury bromide was made symmetrical with sodium stannite and dialkyl mercury was treated with the mercury salt of the monoethyl ester of the d-tartaric acid. The organic mercury diastereomers obtained were separated by crystallization and the residue of the optically active acid in the diastereomer was substituted by bromine by the effect of CaBro

card 1/3

Letters to the Editor

SOV/62-59-4-39/42

 $(R_1R_2R_3C)_2Hg + (C_2H_5OOCCHOHCHOHCOO)_2Hg \longrightarrow 2R_1R_2R_3C -$ - $HgOOCCHOHCHOHCOOC_2H_5 \longrightarrow (mixture of 2 diastereomers)$

CaBr₂:

(after diastereomer R₁R₂R₃C - HgBr + R₁R₂R₃C - HgBr separation)

R₁R₂R₃C - HgBr + R₁R₂R₃C - HgBr antipode (II)

The antipodes have the following specific rotation (in chloroform; c = 1.7; 1 = 1):

 $CH_3CH(HgBr)CH_2CH_3$: (I) $[a]_D^{18} + 10.7^{\circ} \pm 0.8^{\circ}$; (II) $[a]_D^{18} - 10^{\circ} \pm 1.0^{\circ}$

 $\text{CH}_{3}\text{CH}(\text{HgBr})\text{CH}_{2}\text{CH}_{2}\text{CH}(\text{CH}_{3})_{2}: (I) [\alpha]_{D}^{18}-41.6^{\circ}\underline{+}5^{\circ};$ $(II) [\alpha]_{D}^{18}+25^{\circ}\underline{+}2.0^{\circ}$

It might be quite possible that we did not obtain a complete but only a partial separation of the racemates. Also, it is obvious that in the second case we did not obtain the antipode (II) in a pure state. It has to be noted that the possibility of the existence of constant organic mercury antipodes follows from the results of our previous investigations on the preparation of organic mercury diastereomers

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Letters to the Editor

sov/62-59-4-39/42

distinguished only by the configuration of the carbon atom combined with mercury (Ref 1)." There are 3 Soviet references.

ASSOCIATION:

Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova

(Moscow State University imeni M. V. Lomonosov)

SUBMITTED:

December 17, 1958

Card 3/3

5(3) AUTHORS:

Nesmeyanov, Nik. A., Reutov, O. A.

TITLE:

The Derivatives of 1-Carboxyferrocene-1'-Sulfonic Acid (Proizvodnyye 1-karboksiferrotsen-1'-sul'fonovoy kisloty)

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 5, pp 926-929 (USSR)

sov/62-59-5-27/40

ABSTRACT:

In an earlier paper (Refs 1,2) the authors synthetized a number of ferrocene carboxylic acids of the general formula Y-C₅H₄-Fe-C₅H₄-COOH, and on this basis they investigated the influence exercised by the substituent Y upon the acetic character of ferrocene carboxylic acid. The same influence was investigated also in the present paper, but stronger electronegative substituents were used. For this purpose, the ferrocene carboxylic acid and its methyl ester were sulfonated and the derivatives of the acid already mentioned in the title were investigated. The following 10 derivatives were obtained: $F < \frac{\text{COOH}}{\text{SO}_3} \text{ (I)}; F < \frac{\text{COCl}}{\text{SOCl}_2} \text{ (III)}; F < \frac{\text{CONH}_2}{\text{SO}_2} \text{ (III)}; F < \frac{\text{COOH}}{\text{SO}_2} \text{ (IV)};$

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SOV/62-59-5-27/40
The Derivatives of 1-Carboxyferrocene-1'-Sulfonic Acid

$$F < {}^{SO_3H}_{COOCH_3}$$
 (V); $F < {}^{COOCH_3}_{SOC1_2}$ (VI); $F < {}^{COOCH_3}_{SO_2F}$ (VII); $F < {}^{COOCH_3}_{SO_2NH_2}$ (VIII); $F < {}^{COOCH_3}_{SO_2NH_2}$

The dissociation constants of several acids (IV, IX) were determined and compared with those of reference 2. This showed that by the presence of a sulfamide substituent the acidity of ferrocene carboxylic acid is increased 5.5-fold and by that of a sulfofluoride substituent even 9-fold (Table 2). This is indicative of the considerable influence exercised by the substituent upon the carboxyl group, which is on the other ring of the ferrocene molecule. There are 1 table and 2 Soviet references.

ASSOCIATION:

Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova

(Moscow State University imeni M. V. Lomonosov)

SUBMITTED:

September 10, 1958

Card 2/2

CIA-RDP86-00513R001444710019-0 "APPROVED FOR RELEASE: 06/20/2000

.5(3) AUTHORS:

Reutov, O. A., Shatkina, T. N.

sov/62-59-9-37/40

TITLE:

Rearrangement of the Free Propyl Radical

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 9, pp 1690-1691 (USSR)

ABSTRACT:

The authors found that the free propyl radical formed by thermal decomposition of n-butyric peroxyde in CCl, by rearrangement can

change the position of the carbon atoms in the chain:

CH3-CH2-CH2-CH2-CH2-CH3 . The rearrangement was verified in the following manner: n-butyric peroxide, tagged with C14 at the ∞-carbon atom, was decomposed in boiling CCl4. The propyl chloride

thus obtained was hydrolyzed to give propanol which was then oxidized to propionic acid by means of potassium permanganate. Potassium dichromate decomposed propionic acid to acetic acid. Rearrangement could not be observed at the stage of propyl chloride hydrolysis, and must therefore have taken place in the

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Rearrangement of the Free Propyl Radical

SOV/62-59-9-37/40

carbon chain. This is the first time a rearrangement has been

observed in simple hydrocarbons.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova, Khimicheskiy fakul tet (Moscow State University imeni M. V. Lomonosov, Department of Chemistry). Akademiya meditsinskikh nauk

SSSR (Academy of Medical Sciences, USSR)

SUBMITTED:

June 15, 1959

Card 2/2

CIA-RDP86-00513R001444710019-0" **APPROVED FOR RELEASE: 06/20/2000**

SOV/62-59-9-38/40 5(3) Reutov, O. A., Uglova, E. V. AUTHORS: Stereochemistry of Electrophilic Substitution at Saturated TITLE: Carbon Atoms Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, PERIODICAL: 1959, Nr 9, p 1691 (USSR) By investigating the antipodes of asymmetric organomercury compounds the authors (Ref 1) found that the stereochemical ABSTRACT: configuration of these compounds is retained in substitution at the electrophilically bound asymmetrical carbon atom. This was also observed in the case of 1,4-dimethylpentylmercury bromide, which reacts with magnesium-organic compounds under the influence of HgBr2 or HBr and gives the same 1,4-dimethylpentylmercury bromide with $[\alpha]_{n}^{18} - 18 + 1.1^{\circ}$ with $[\alpha]_D$ = 10=10. $(CH_3)_2$ CHCH $_2$ CH $_2$ CH $_3$ CH $_3$ CHCH $_3$ CHCH $_2$ CH $_3$ CHCH $_4$ CH $_2$ CH $_3$ CHCH $_4$ CH $_3$ CHCH $_4$ CH $_4$ CH $_4$ CH $_4$ CH $_4$ CH $_5$ CHCH $_3$ CHCH $_4$ CH $_4$ CHCH $_3$ CHCH $_4$ CHCH $_4$ CHCH $_3$ CHCH $_4$ CHCH $_4$ CHCH $_5$ CHCH $_$ Card 1/2

CIA-RDP86-00513R001444710019-0 "APPROVED FOR RELEASE: 06/20/2000

Stereochemistry of Electrophilic Substitution at

SOV/62-59-9-38/40

Saturated Carbon Atoms

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova Khimicheskiy fakul tet (Moscow State University imeni M. V.

Lomonosov, Department of Chemistry)

SUBMITTED:

June 15, 1959

Card 2/2

G. : HUNGARY Organic Chemistry, General and Theoretical COUNTRY CATEGORY Problems of Organic Chemistry 1960, No. 1088 : RZKhim., No. 1 ADS. JOUR. Reutow, O. A. AUTHOR Hungarian AS : Investigations of the Mechanisms of Some Sub-THST. stitution Reactions with the Use of Labeled TITLE : Acta chim. Acad. scient. hung., 1959, 18, Atoms ORIG. PUB. No 1-4, 439-148 : A review report on the works of the author is ABSTRACT given. The discussion bears on the reactions of isotopic exchange of R2Hg and RHgX (R = alicyl, X = halide) with Hg203 (homolytic substitution reactions), the reactions of isotopic exchange of RHgX with Hg203X₂ (electrophilic substitution reactions), the influence of structural factors and conditions of the reaction, the stereochemistry of homolytic and 1/2 CAPD: 2/2 CARD: G-1 APPROVED FOR RELEASE: 06/20/2000 CIA-RDP86-00

Reutov, O. A., Lu Chinada hada sov/79-29-1-39/74 AUTHORS:

Stereochemistry of the Reaction of 3-Bromo-Mercury-1-Camphor TITLE:

and 3-Bromo-Mercury-d-Camphor With Sodium Thiosulfate

(Stereokhimiya reaktsii 3-brommerkur-l-kamfory i 3-brommerkur-

d-kamfory s tiosul'fatom natriya)

Zhurnal obshchey khimii, 1959, Vol 29, Nr 1, pp 182-187 (USSR) PERIODICAL:

According to reference 1 it was determined that the symmetrization of diastereomeric 1-methyl esters of the d-bromo-ABSTRACT:

mercury-phenyl acetic acid with ammonia in chloroform represents a reaction of electrophilic substitution character on the saturated carbon atom and proceeds by maintaining the stereochemical structure. The investigation of the kinetics of this reaction indicated (Ref 2) that it proceeds in two steps (Scheme 1). The first step (a) is a reaction of bimolecular electrophilic substitution character. In connection with that the present paper describes the results of the further

investigation of the stereochemistry of symmetrization reaction, on the basis of organomercury derivatives of camphor. The

mixture of the diastereomers of 3-bromomercury-1-camphor and the mixture of the diastereomers of 3-bromomercury-d-camphor Card 1/2

sov/79-29-1-39/74

Stereochemistry of the Reaction of 3-Bromo-Meroury-1-Camphor and 3-Bromo-Mercury-d-Camphor With Sodium Thiosulfate

were obtained by mercurization of 1- and d-camphor by means of K2HgJ (Ref 3). From the first mixture two diastereomers of 3-bromomercury-1-camphor were separated by fractional recrystallization, which differ in the structure of the α -carbon atom (I and II). From the second mixture the diastereomers of 3-bromomercury-d-camphor (III) and (IV) were separated. (I) and (III) are more stable than (II) and (IV). Sodium thiosulfate and hydrazine hydrate proved to be the only symmetrizing agents for all organo-mercury compounds, since with other agents (KJ, KOH, KCNS, Na2S, and Na2SnO2) a cleavage of all C-Hg bonds took place. The transforations of the organomercury derivatives of 1-and d-camphor may be represented summarily by the scheme 2. Thus, the reaction proceeds by maintaining the structure. There are 4 references, 2 of which are Soviet.

Moskovskiy gosudarstvennyy universitet (Moscow State University) ASSOCIATION:

SUBMITTED:

October 28, 1957

Card 2/2

CIA-RDP86-00513R001444710019-0"

APPROVED FOR RELEASE: 06/20/2000

5(3) AUTHORS:

Reutov, O. A., Lu Tszin-chzhu

sov/79-29-4-36/77

TITLE:

On the Stereochemistry of the Symmetrization Reaction of Some Organo-mercury Derivatives of Camphor Under the Influence of Hydrazine Hydrate (O stereokhimii reaktsii simmetrizatsii nekotorykh rtutnoorganicheskikh proizvodnykh kamfory pod deystviyem gidrazin-gidrata)

PERIODICAL:

Zhurnal obshchey khimii, 1959, Vol 29, Nr 4, pp 1207-1213 (USSR)

ABSTRACT:

Having previously examined the stereochemistry of the symmetrization reaction of 3-bromine-mercury camphor under the influence of sodium thiosulfate (Ref 1) the authors tried in the present case to perform the same reaction under the influence of hydrazine hydrate. In the article under review the constants of hydrazine hydrate of 3-bromine-mercury-1-camphor and 3-bromine-the diastereomers of 3-bromine-mercury-1-camphor and 3-bromine-mercury-d-camphor (I), (II), (III), and (IV) obtained earlier (Ref 1) are listed. The diastereomers (I), (II), and (III) were used in the experiments reported on below. The reaction follows the scheme 1:

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sov/79-29-4-36/77

On the Stereochemistry of the Symmetrization Reaction of Some Organo-mercury Derivatives of Camphor Under the Influence of Hydrazine Hydrate

(details of this synthesis in the experimental part). For the time being this reaction was thus tested on the two diastereomers of 3-bromine-mercury-1-camphor and on one of the diastereomers of 3-bromine-mercury-d-camphor under the influence of hydrazine hydrate. In all cases the racemization of the configuration was found in the α -carbon atom. This effect may be due either to the stereochemical reaction of symmetrization as such or to the racemization of the organo-mercury end products under the influence of an agent of basic character (hydrazine hydrate). At the contact with a small amount of hydrazine hydrate in dioxane the less stable diastereomer of 3-bromine-mercury-1camphor is isomerized and forms the stabler diastereomer.

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sov/79-29-4-36/77

On the Stereochemistry of the Symmetrization Reaction of Some Organo-mercury Derivatives of Camphor Under the Influence of Hydrazine Hydrate

3-methyl-, 3-ethyl-, and 3-benzyl-3-bromine-mercury camphor were synthesized. The symmetrization of 3-benzyl-3-bromine-mercury camphor under the influence of ammonia was investigated. There are 3 references, 2 of which are Soviet.

ASSOCIATION:

Moskovskiy gosudarstvennyy universitet (Moscow State University)

SUBMITTED:

March 18, 1958

Card 3/3

307/79-29-5-44/75 5 (3) Reutov, O. A., Ostapchuk, G. M. AUTHORS: The Reaction of the Isotopic Exchange Between Aryl-mercury Chlorides and Metallic Mercury Marked by Hg 203 (Reaktsiya TITLE: izotopnogo obmena erilmerkurokhloridov s metallicheskov rtut'yu, mechennoy Hg 203) Zhurnal obshchey khimii, 1959, Vol 29, Nr 5, PERIODICAL: pp 1614-1617 (USSR) In a previous paper (Ref 1) the following reaction was described: $(p-XC_6H_4)_2Hg + Hg \longrightarrow (p-XC_6H_4)_2Hg + Hg$. The ABSTRACT: reaction rate depended on the substituent X and increased in the following order: 0_2 H < 0_2 H < 0_2 H < 0_3 H < present paper investigates the reaction p-XC6H4-HgCl + Hg \interpretation p-XC6H4-HgCl + Hg. It took place in a solution of arylmercury chloride in anhydrous pyridine at 60° and at 1500 rpm/min approximately of the mixer. After certain intervals samples were taken, the colloidal mercury centrifuged off, the aryl-mercury-chloride precipitated by means of water card 1/3

The Reaction of the Isotopic Exchange Between SOV/79-29-5-44/75 Aryl-mercury Chlorides and Metallic Mercury Marked by Hg²⁰³

acidified with hydrochloric acid, filtered and recrystallized. The substance dissolved again in organic liquid (chloroform, acetone) was dropped on a standard filter, and this thin layer coated with plexiglass lacquer. The radioactivity was determined by means of the counter MS-4. The results of repeated experiments are given in a table. The authors observed a reaction rate higher than that of diaryl compounds as well as an increase in the reaction rate in the order $O_2H < C_2H_5OCO < CI < H, CH_3$. Since free radicals are not formed in monoaryl compounds even by irradiating the solution with ultraviolet light, the reaction mechanism is explained by the formation of a four-membered, activated complex:

Ar-Hg-Cl + Hg Ar-Hg-Cl + Hg.

There are 1 table and 2 references.

Card 2/3

CIA-RDP86-00513R001444710019-0 "APPROVED FOR RELEASE: 06/20/2000

Anyl-mercury Chlorides and Metallic Mercury Marked by Mg203

Moskovskiy gosudarstvennyy universitet (Moscow State ASSOCIATION:

University)

April 9, 1958 SUBMITTED:

Cara 3/3

5 (3) AUTHORS:	Reutov, C. A., Lu Ching-Chu Scv//9-29-5-45/75	
TITLE:	Stereochemistry of the Symmetrization Reactions of 2-Chloro- mercury Camphane Under the Influence of Hydrazine Hydrate and Sodium Stannite (Stereokhimiya reaktsiy simmetrizatsii 2-khlormerkurkamfana pod deystviyem gidrazin-gidrata i stannita natriya)	
PERIODICAL:	Zhurnal obshchey khimii, 1959, Vol 29, 3r 5, pp 1617-1626 (USSR)	
ADSTRACT:	Ouring the investigation of the symmetrization of 3-bromomercury-camphor under the influence of hydrazine hydrate def 1) a racemization was found to take place in all experiments (the authors emphasize that the expressions experiments of "maintenance of the configuration" always experiments with 3-alkyl-3-bromomercury derivatives of	

Stereochemistry of the Symmetrization Reactions of SOV/79-29-5-45/75 2-Chloro-mercury Camphane Under the Influence of Hydrazine Hydrate and Sodium Stannite

camphor were unsuccessful. The experiments were carried cuby the authors with mercury compounds of camphane which was formed from a-pinene. The 2-chloro-mercury-camphanes obtained, however, yielded a difficultly separable mixture of stereomers. Therefore f-b-pinene was chosen as initial stereomers. Therefore for the synthesis of 2-chloro-mercury-camphanes which differ only by the configuration of the second carbon which differ only by the configuration of the second carbon atom. By the action of hydrogen chloride bornyl chloride was obtained, and therefrom the mixture of two diastereomers of 2-chloro-mercury-camphane was formed. The diastereomer I

isolated therefrom gave [a] 18 - 10.1 ± 1.10, the diastereomer II: [a] 18 + 15.4 ± 1.20. The diastereomer I

reacts with hydrazine hydrate under the formation of unstable mercury-bis-camphane which separates metallic mercury already at low temperature. This bis-camphane is an already at low temperature. With hydrochloric acid and ethanol individual diastereomer. With hydrochloric acid and ethanol the pure diastereomer I of 2-chloro-mercury-camphane is

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Stereochemistry of the Symmetrization Reactions of SOV/79-29-5-45/75 2-Chloro-mercury Camphane Under the Influence of Hydrazine Hydrate and Sodium Stannite

formed again from it. The reaction thus proceeds under the maintenance of the configuration of the C-atom in position 2. The symmetrization of the diastereomer II was carried out in the same way. After splitting the bis-compound the pure diastereomer I is obtained. The diastereomer II is unstable, accordingly, and is transformed into the I-form. With sodium stannate the same reactions were obtained. The maintenance of the configuration unusual for the radical substitution is probably due to the fact that no optical antipodes are concerned but diastereomers which exhibit antipodes are concerned but diastereomers which exhibit reactions performed and gives the data of the resultant reactions performed and gives the data of the resultant compounds. There are 10 references, 5 of which are Soviet.

SUBMITTED:

Warch 29, 1958

Card 3/3

sov/76-33-1-25/45

5(4) AUTHORS: Reutov, O. A., Beletskaya, I. P., Hardaleyshvili, R. Ye.

TIPLE:

Reaction Kinetics of the Symmetrization of Organo-Mercury Salts (Kinetika reaktsii simmetrizatsii rtutnoorganicheskikh soley). I.Determination of the Order From the Organo-Mercury Salt of the Reaction of the Symmetrization of Esters of a-Mercury Bromide Phenylacetic Acid Under the Influence of Ammonia (I. Opredeleniye poryadka po rtutnoorganicheskoy soli reaktsii simmetrizatsii efirov a-brommerkurfeniluksusnoy kisloty pod deystviyem ammiaka)

PERIODICAL:

Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 1,

pp 152 - 155 (USSR)

ABSTRACT:

On the example of the diastereomeric 1-menthyl esters of the a-mercury bromide phenyl acetic acid (I) it had already been found earlier (Ref 1) that the symmetrization of organo-mercury salts with ammonia proceeds with a constant stereochemical structure. Winstein (Uinshteyn)(Ref 2) obstereochemical structure winstein (Uinshteyn) (Ref 2) obtained the same results on experiments with a different salt, whereas Hughes and Ingold (Kh'yuz and Ingol'd) assumed that an electrophilic substitution takes place with a constant

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Reaction Kinetics of the Symmetrization of Organo-SOV/76-33-1-25/45 Reaction Kinetics of the Symmetrization of Organo-Mercury Salt Mercury Salts. I. Determination of the Order From the Organo-Mercury Salt Mercury Salts. I. Determination of the Order From the Organo-Mercury Salt Mercury Bromide Phenylof the Reaction of the Symmetrization of Esters of α -Mercury Bromide Phenyloctic Acid Under the Influence of Ammonia

structure in the mechanism S_E^1 and a change of the structure in S_E^2 . Since a progress of the reaction mentioned in the title is doubtful with S_E^2 , the reaction kinetics of ethylene and 1-menthyl ester of (I) was investigated with ammonia in the case under discussion. The symmetrization of in the case under discussion. The symmetrization of $R_1R_2R_3$ CHgX (R_1 = C_6H_5 , R_2 = H, R_3 = $COOC_1OH_19$) took place in absolute chloroform, mixed with ammonia, at 20°. The nephelometric measuring method was used. The concentration of the substances was in the range of $(6.8-0.85)\cdot 10^{-5}$ mol/ml. The reaction order of $R_1R_2R_3$ CHgX was determined by the kinetic curves and the initial concentration of (I). The experimental results obtained showed that the symmetrization reaction of $R_1R_2R_3$ CHgX is of the second order. There are 4 figures, 1 table, and 3 references, 1 of which is Soviet.

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Reaction Kinetics of the Symmetrization of Organo-SOV/76-33-1-25/45 Mercury Salts. I. Determination of the Order From the Organo-Hercury Salt of the Reaction of the Symmetrization of Esters of α -Mercury Bromide Phenylacetic Acid Under the Influence of Ammonia

ASSOCIATION:

Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova

(Moscow State University imeni M. V. Lomonosov)

SUBMITTED:

July 4, 1957

Card 3/3

5(4)
AUTHORS: Reutov, O. A., Beletskaya, I. P., Mardaleyshvili, R. Ye.

TITLE: Kinetics of the Symmetrization Reaction of Organomercury Salts.

II. Determination of the Reaction Order of Symmetrization With Ammonia of the Esters of α-Bremo Mercuro Phenyl Acetic Acid

With Respect to Ammonia

PERIODICAL: Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 9, pp 1962-1968

(USSR)

ABSTRACT: In follow-up of a previous report (Ref 1), further investi-

gations were made here concerning the reaction mentioned in the title, with special regard to the reaction order with respect to ammonia (I) as well as the influence exerted by (I) concentration and various additions upon the rate and intensity

of symmetrization. Experiments were made in a test tube (Fig 1) with 1.36.10⁻³ mol of organomercury salt (II) and (3.28, 2.76, 2,12, 1.60, 1.07).10⁻³ mol (I). The reaction was stopped at various time intervals by the addition of an excess of 0.149 n

HCl (with respect to the (I)-encunt), and the acid excess was titrated (Table 1). The order of reaction with respect to (I)

Card 1/3 was determined from the initial reaction rate of (I) as a

Kinetics of the Symmetrization Reaction of Organomercury Salts. II. Determination of the Reaction Order of Symmetrization With America of the Esters of α -Bromo Mercuro Phenyl Acetic Acid With Respect to Ammeria

function of its initial square concentration (Tables 2,3). Nephelometric measurements were likewise made, and the values for I = f(t) are tabulated (Table 4). In both cases, a direct dependence of the initial reaction rate on the initial square concentration of (I) was ascertained. In the symmetrization of (II), (I) is, under prevailing conditions, consumed according to the second order. From the curves I = f(t) the portion of reacted (II) was found to lapend upon the various initial concentrations of (I) (Table 5); it was further ascertained with the titration method that in the case of (II) amounting to 1.36.10-2 mol and (I) lying below 4.30.10-3 mol, the reaction intensity is determined by the initial concentration of (I) (Table 6). Additions of a symmetrical compound (R1R2R3C-)2Hg (formed in the course of reaction) (Table 7) showed that when increasing the concentration of these additions the reaction rate is lowered. The symmetrization reaction under investigation is assumed to take place in two stages (1) and (2), where (1) is a bimolecular electrophilic substitution in the

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APPROVED FOR RELEASE: 06/20/2000 CIA-RDP86 00513R001444710019-0 Kinetics of the Symmetrization Reaction of Organomercury Salts. II. Determination of the Reaction Order of Symmetrization With Ammonia of the Esters of α-Bromo Mercuro Phenyl Acetic Acid With Respect to Ammonia

saturated carbon atom. It had already been shown (Ref 2) that the symmetrization in question leaves the stereochemical configuration unaltered; thus, a bimolecular reaction of the mentioned kind with preserved stereochemical configuration was established for the first time. There are 6 figures, 7 tables, and 3 references, 2 of which are Soviet.

SUBMITTED:

February 21, 1958

5(2).

Nesmeyanov, A. N., Academician,

SOV/20-125-6-25/61

Reutov. O. A., Corresponding Member

AS USSR. Tolstaya, T. P., Ptitsyna, O. A.,

Isayeva, L. S., Turchinskiy, M. F.,

Bochkareva, G. P.

TITLE:

Organometallic Compounds Prepared From Double Salts of Halogen Metals and Halogenoniums (Metalloorganicheskiye soyedineniya iz dvoynykh soley galoidnykh metallov i galogenoniyev)

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 125, Nr 6, pp 1265-1268 (USSR)

ABSTRACT:

The present paper adds two further types, (III) and (IV), to the two rather similar reaction types (I) and (II) of the synthesis of organometallic compounds. Hg, Tl, Sn, Pb, As, Sb, and Bi may appear as metal $\mathbf{M}^{(n)}$ in the method of diazonium double salts (Ref 1); Cu, Zn, Fe, as well as $\mathbf{M}^{(p)} = \mathbf{M}^{(n)}$ as metal $\mathbf{M}^{(p)}$ for various combinations. In the method of iodonium double salts (Ref 2) Hg, Sn, Sb, and Bi were investigated as $\mathbf{M}^{(n)}$ which gave a good yield of corresponding organometallic

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Organometallic Compounds Prepared From Double Salts SOV/20-125-6-25/61 of Halogen Metals and Halogenoniums

compounds. The same metal M(n) is usually used as M(p), sometimes, however, Zn or Gu. The corresponding decomposition reactions were carried out by the authors in an acetone solution. For this purpose the same metal powder was used as was chosen by O. A. Reutov and O. A. Ptitsyna for diphenyl iodonium salts. The course and the results of these new reactions were found to be completely similar to those of the last-mentioned salts. This is a new confirmation of a similarity of all diaryl halogenoniums. Phenyl mercury iodide with yields of 22 and 35% is produced by decomposition of the double salts of diphenyl chloronium iodide and of diphenyl bromonium iodide with HgJ₂ by powdered copper in acetone at low temperature. Diphenyl-tin-dichloride with yields of 57 and 55% is produced by decomposition of the double salts of diphenyl chloronium- and diphenyl bromonium with SnCl₄ by powdered tin. The decomposition of the corresponding double salts of antimony powder leads to a mixture

of phenyl-dichlorostibine, diphenyl-chlorostibine, and a small quantity of organo-antimony triaryl compounds. Triphenyl bismuth is produced by decomposition of the bismuth-trichloride

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Organometallic Compounds Prepared From Double Salts SOV/20-125-6-25/61 of Halogen Metals and Halogenoniums

double salts by bismuth powder. According to the analysis it is assumed that the double salts of antimony-trichloride and of bismuth-trichloride form mixtures of the compounds: $\left[\left(C_6 H_5 \right)_2 Ha1^+ \right] MeC1_4^-$ and (C6H5)2Hal MeCl5. Table 1 gives 21 decomposed salts, the decomposition temperature and calculated as well as actually obtained results of the analysis, table 2 shows the decomposition reactions of the aforesaid double salts with the halides of heavy metals. The double salts of triphenyloxonium either do not react at all with the metal powders under the given experimental conditions, or only with a change of the anion part of the double salt. The cation of triphenyl-oxonium is not changed and does not form organometallic compounds. Thus this method is restricted by the inapplicability of oxoniumand (as is expected by analogy) of ammonium salts. The authors finally try to explain this behavior of triphenyl-oxonium salts. There are 2 tables and 11 references, 5 of which are Soviet.

ASSOCIATION: Card 3/4 Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova (Moscow State University imeni M. V. Lomonosov) Institut

Organometallic Compounds Prepared From Double Salts SOV/20-125-6-25/61 of Halogen Metals and Halogenoniums

elementoorganicheskikh soyedineniy Akademii nauk SSSR (Institute of Elemental-Organic Compounds of the Academy of Sciences USSR)

SUBMITTED: January 7, 1959

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D048/D006

AUTHOR:

Reutov, O.A., Corresponding Member

TITLE:

The World's Largest School of Metal-Organic Chemists

PERIODICAL:

Priroda, 1960, Nr 4, pp 43 - 48 (USSR)

ABSTRACT:

On 9 Sep 1959, the 60th birthday of A.N. Nesmeyanov, President of the Akademiya nauk SSSR (Academy of Sciences of the USSR) and his decoration with the Order of Lenin were celebrated. In the present article, the author gives historical data on the development of the synthesis of metal-organic compounds and elucidates A.N. Nesmeyanov's main works on organic chemistry. Nowadays, 15,000 metal-organic compounds are known, of which tetraethyl lead (TEL) ranks first. Lithium— and aluminum—organic compounds are used as catalysts in the production of plastics, and tin-organic compounds as anticorrosive admixtures, plastics stabilizers, catalysts for vulcanization of caoutchouc, bactericides, and fungicides. A.N. Nesmeyanov, and a collective

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The World's Largest School of Metal-Organic Chemists

of the Vsesoyuznyy nauchno-issledovatel'skiy khimiko-farmatsevticheskiy institut imeni S. Ordzhonikidze (All-Union Scientific Chemical and Pharmaceutical Research Institute imeni S. Ordzhonikidze)
has developed a preparation called "diotsid" which
possesses an extremely high bactericidal capability.
This preparation can be effectively used by surgeons
for quick disinfection of their hands prior to operating. Russian chemists A.M. Butlerov, A.M. Zaytsev,
S.N. Reformatskiy, N.D. Zelinskiy, Zh.I. Iotsich,
and V.V. Chelitsev made valuable contributions to the
development of metal-organic chemistry. A.N. Nesmeyanov developed a perfect method of synthesizing
metal-organic compounds of heavy metals, known as
"Nesmeyanov's diazomethod". The essence of this
method is explained by an example of synthesizing
mercury-organic compounds. The reaction occurs according to the following formula:

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 $RN_2Cl \cdot HgCl_2 + 2Cu \rightarrow R - Hg - Cl + N_2 + Cu_2Cl_2$

With the aid of this reaction, Nesmeyanov and his pupils obtained various organic compounds of mercury, thallium, germanium, tin, lead, arsenic, atnimony and bismuth. Hundreds of substances, formerly inaccessible, are now to be obtained by this method. Another synthesis developed in Nesmeyanov's school is the method of mutating one kind of metal-organic compounds into another. The most important of them is the change of mercury-organic into metal-organic compounds of other metals. In nearly all cases the reverse mutation of the metal compounds into mercury-organic compounds has been found. Besides this, Nesmeyanov worked out fundamental theoretical problems of organic chemistry on the basis of metal-organic compounds. The author describes three trends of Nesmeyanov's theoretical works: 1) tautomerism and the

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reactivity of organic compounds; 2) the mechanism of the reactions of carbon atom substitution; 3) the mechanism of formation and disruption of metal combinations - carbon and several other chemical combinations. A.N. Nesmeyanov has proved that double reactivity is not always conditioned by tautomerism but may also depend on other causes. He found and studied several cases of double reactivity when tautomerism was ab-With the aid of theoretical calculations, M.I. Kabachnik has shown that, in general, a pseudorism of molecules does not exist. The results of this work have shown that double reactivity may be caused by special properties in the reacting molecule. In work on the mechanism of the reaction of substitution in a carbon atom, the problems of the stereochemistry of these reactions rank first. Nesmeyanov's school was very successful in explaining the nature of substitution in a carbon atom. The study of the stereo-

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chemistry of substitution in an ethylene carbon atom showed that both the electrophylic and the homolytic substitions proceeded while the geometrical configuration was maintained (A.N. Nesmeyanov and A.Ye. The value of the work on the mechanism of Borisov). reaction consists in making use of the data obtained for guiding organic reactions in a desired direction. A.N. Nesmeyanov carried out radical and ion breakdown of diazo-compounds and diaryliodonium salts. Each of these types of breakdown has its special features and advantages for the synthesis of metalorganic or organic compounds. The author gives an example of ion breakdown of aryldiazo salts in a medium of chlorobenzene or bromobenzene, which opened the way to the synthesis of organic derivative polyvalent chlorine and bromine. The work on the chemistry of ferrocene (dicyclopentadienyl-iron) has a special place in Nesmeyanov's investigations. The iron-organic compound, discovered 8 years ago,

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is extremely resistant and resembles benzene in many chemical properties. Nesmeyanov's school obtained dozens of ferrocene compounds which may serve as antidetonators, semi-conductors, initial substances for synthesizing polymers, etc. One of the most interesting subjects of Nesmeyanv's investigations in the field of element-organic compounds is the synthesis of "onium" salts (diphenylchloronium and diphenyl-bromonium salts), a direct development of the diazomethod. At the same time, these investigations were connected with his work in the field of organic compounds containing elements in an unusual valent state. Nesmeyanov's investigations into telomerization resulted in the development of the new synthetic fibers "enant" and "pelargon" which are in many ways superior to capron and nylon. Nowadays, A.N. Nesmeyanov heads the world's largest school of metal-organic chemists at the Institut elementoorganicheskikh

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741 \$/026/60/000/04/019/070 D048/D006 The World's Largest School of Metal-Organic Chemists soyedineniy AN SSSR (Institute for Element-Organic Compounds of the AS USSR) and the Moskovskiy gosudarstvennyy universitet imeni M.V. Lomonosova (Moscow State University imeni M.V. Lomonosov). Many of Nesmeyanov's famous pupils, including M.I. Kabachnik, Corresponding Member of the AS USSR, R.Kh. Freydlina, Corresponding Member of the AMN, N.K. Kochetkov, Doctor of Medical Sciences, A.Ye. Borisov and others are now heads of important scientific institutions. The following important Soviet centers for investigating metal-organic chemistry are mentioned in this article: the Gor'kovskiy gosudarstvennyy universitet (Gor'kiy State University); the Fiziko-khimicheskiy institut imeni L.Ya. Karpova (Physical and Chemical Institute imeni L.Ya. Karpov) in Moscow. G.A. Razuvayev, head of the Gor'kiy University leads investigations into metal-organic compounds of heavy metals. The main subject of these investigations is the breakdown of metal-organic compounds which results Card 7/9

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in the formation of free radicals in solutions. Razuvayev developed several original methods of synthesizing metal-organic compounds, such as the method of synthesizing mercury-organic compounds from organic perioxide and from mercury salts of organic acids. The work of the Physical and Chemical Institute is above all concentrated on compounds of 3rd and 4th group metals of the periodic system and on lithium-organic compounds. The Institute is headed by K.A. Kocheshkov, Nesmeyanov's former co-worker. The latest results in the chemistry of metallocene and carbonyls indicate that metal-organic compounds

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are important as intermediate substances in industrial catalytic processes. There is 1 photograph and 3 references of which 2 are Soviet and 1 English.

SSOCIATION: AN SSR (AS USSR)

Card 9/9

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CANADA CONTRACTOR OF THE CONTR	. Moskovskiy gosudarstvennyy universitet im. (Diazonium compounds)	M.V. Lomonosova.
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APPROVED FOR RELEASE: 06/20/2000 CIA-RDP86-00513R001444710019-0"

S/062/60/000/009/020/021 B023/B064

AUTHORS:

1. Reutov, O. A. and Beletskaya, I. P.; 2) Reutov, O. A. and Lovtsova, A. N.; 3. Vinogradova, L. P. and Zav'yalov, S.I.

TITLE:

1. Electrophilic and Radical Substitution of Iodine for the Mercury Atom in Organo-mercury Salts. 2. Introduction of Dichloro Carbene Into the Metal - Haloid Binding. 3. Interaction of 2-Formyl Cycloalkanones With Hydrogen Peroxide

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicneskikh

nauk, 1960, No. 9, pp. 1716-1717

TEXT: 1. In the course of their studies of the mechanism of the electrophilic substitution on the saturated carbon atom, the authors investigated the reaction of the organo-mercury salts: athyl ester of α -bromo mercury phenyl acetic acid (I) and the benzyl mercury bromide (II) with iodine. The electrophilic substitution of the mercury atom was carried out under the action of iodine in cadmium iodide solution. The reaction took place

in aqueous dioxan: R - HgBr + $I_2 \xrightarrow{\text{CdI}_2} R - I + \text{HgBr I}$.

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1. Electrophilic and Radical Substitution of Iodine for the Mercury Atom in Organo-mercury Salts. 2. Introduction of Dichloro Carbene Into the Metal - Haloid Binding 3 Interaction of 2-Formyl Cycloalkanones With Hydrogen Peroxide

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In case (I) the reaction proceeds rapidly, in case (II) much slower. The reaction kinetics of (II) with iodine was spectrophotometrically recorded and examined by the titration method. The reaction proceeds rapidly in the presence of CdI₂, i.e., photochemically by the radical mechanism. The reaction of (I) with iodine in the absence of CdI₂ (radical reaction) is of first order with respect to iodine and of zeroth order with respect to the organo-mercury salt. The kinetics was spectrophotometrically recorded. Finally, a very important effect of the structural factor upon the rate of the electrophilic and radical substitution of the iodine atom for the mercury atom on saturated carbon was determined. 2. The authors found that the dichloro carbene forming in the benzene medium under the action of tertiary potassium butylate upon chloroform, is capable of linking itself into the mercury - chlorine binding under the formation of trichloro methyl mercury compounds. Sublimate reacts with dichloro carbene under the formation of trichloro methyl mercury chloride (melting point 180°).

1. Electrophilic and Radical Substitution of Iodine for the Mercury Atom in Organo-mercury Salts. 2. Introduction of Dichloro Carbene Into the Metal - Haloid Binding. 3. Interaction of 2-Formyl Cycloalkanones With Hydrogen Peroxide

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Found: Hg 56.83%. Calculated: Hg 56.60%. Phenyl mercury chloride forms trichloro methyl phenyl mercury (melting point 113.5-114°). Trans-β-chloro vinyl mercury vinyl mercury chloride forms trichloro methyl-trans-β-chloro vinyl mercury (melting point 80-81°). Found 53.06%. Calculated: 52.72%. The latter compound is converted under the action of chlorine or bromine into trichloro pound is converted under the action methyl mercury bromide, respectively. Methyl mercury chloride or trichloro methyl mercury bromide, respectively. At present, the authors are investigating the possibility of synthesizing at present, the authors found that under the action of hydrogen peroxide carbene. Σ. The authors found that under the action of hydrogen peroxide at low temperatures 2-formyl cyclopentanone and 2-formyl cyclohexanone undergo an oxidative splitting and yield adipic and pimelic acid, undergo an oxidative splitting and yield adipic and pimelic acid, respectively. This rare reaction of 2-formyl cycloalkanones may be used for the production of a variety of dicarboxylic acids, beginning with the cyclic ketones. There are 2 Soviet references.

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1. Electrophilic and Radical Substitution of S/06 Iodine for the Mercury Atom in Organo-mercury BO23 Salts. 2. Introduction of Dichloro Carbene Into the Metal - Haloid Binding. 3. Interaction of 2-Formyl Cycloalkanones With Hydrogen Peroxide

S/062/60/000/009/020/021 B023/B064

ASSOCIATION:

Moskovskiy gosudarstvennyy universitet im. M.V. Lomonosova (Moscow State University imeni M. V. Lomonosov), (Reutov,O.A., Beletskaya, I. P., Lovtsova, A. N.), Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences USSR) (Vinogradova, L. P. and Zav'yalov, S.I.)

SUBMITTED:

1. May 23, 1960; 2. June 9, 1960; 3. June 13, 1960

Card 4/4

REUTON O.A.

S/078/60/005/05/36/037 B004/B016

AUTHORS:

Tananayev, I. V., Luzhnaya, N. P.

TITLE:

The XVII Congress on Pure and Applied Chemistry

PERIODICAL: Zhurnal neorganicheskoy khimii, 1960, Vol. 5, No. 5, pp. 1178 - 1183

TEXT: The XVII Congress of the IUPAC (International Union of Pure and Applied Chemistry) took place in Munich from July 30 to September 6, 1959. It was preceded by the XX Conference of the IUPAC (August 26-29, 1959) which was attended by a Soviet delegation consisting of B. A. Kazanskiy (re-elected as representative of the USSR at the Bureau of the IUPAC), M. M. Shemyakin (elected as a member of the Section of Organic Chemistry), A. P. Vinogradov (elected as Deputy Chairman of the Section of Geochemistry), I. V. Tananayev (elected as a member of the Section of Inorganic Chemistry), Ya. I. Gerasimov, O. A. Reutov. and G. I. Rakhmaninov. Further, I. P. Alimarin was appointed Second Secretary of the Section of Analytical Chemistry. About 2200 delegates attended the Congress. In a plenary session O. A. Reutov delivered a lecture: "The Mechanism of the Formation of Metal-Carbon Bond and Some Considerations on the Reactivity of Organometallic Compounds of Heavy Metals". Centerning the work of the Sections the

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REUTOV. O.A., PTITSYNA, O.A., ORLOV. S.I.

Synthesis of solid aryl diazonium salts from double aryl diazonium salts of ferric chloride. Vest. Mosk. un. Ser. 2: khim. 15 no.2: 47-49 Mr-Ap *60. (MIRA 13:6)

1. Kafedra organicheskoy khimii Moskovskogo universiteta.
(Diazonium compounds) (Iron chloride)